TRANSLATION OF ANNEXES TO IPER

Process for the Coppering or Bronzing of an Object and Liquid Mixtures therefor

The present invention relates to a process for the currentless coppering (copper coating) or bronzing (bronze coating) of an object, in particular a metallic object, more particularly an object of a ferrous material, above all an iron wire, steel wire or a wire-containing aggregate such as for example a wire mesh, with an aqueous bath containing dissolved copper.

The object of coppering or bronzing is not only to protect the surfaces of the objects to be coated by means of the copper-containing coating against corrosion, but also to form a coating that is as uniform, shiny and adherent as possible. In this connection a peel resistance (adherence) on bending a wire for example as well as a layer weight roughly in the range from 0.8 to 24 g/m^2, in particular in the range from 1 to 18 g/m^2, are desired. The coppering or bronzing bath should be suitable for currentless metallising.

US-A-4,954,369 describes the addition of complexing agents for currentless coppering from aqueous alkaline baths. DE-A1-199 18 833 teaches a multistage process for the electrolytic deposition of a metal layer on electrically non-conducting substrates, *inter alia* from an alkaline coppering bath. WO-A2-92/17624 discloses formaldehyde-free coppering baths containing a copper salt, complex-forming agent and reducing agent with a pH value in the range from 3 to 6.9. GB-A-1 425 298 relates to aqueous alkaline copper-plating baths. All these publications describe coppering processes that can be used in particular for printed circuit boards.

Up to now coppering baths for this purpose are known in which the bath is prepared using a pulverulent copper-rich concentrate, water and sulfuric acid. The baths may for example contain apart from copper sulfate, also sodium chloride, a magnesium salt, a brightening agent and optionally further additives. The powder at the same time offers the possibility of holding comparatively high copper contents in the concentrate and thus of transporting comparatively low weights. Water and sulfuric acid are normally available *in situ* or can be obtained nearby. Such pulverulent concentrates often have a copper content in the range from 12 to 22 wt.% Cu. The concentrates are very sensitive to moisture on account of the high content of copper sulfate, and their quality depends in particular on the freedom from or on the nature and amount of the impurities and/or additives. On account of the sensitivity to moisture and the chemical reactions occurring in the powder as a result of the moisture, the storage life of the pulverulent concentrates is often limited. Changes are initially manifested by a green colouration and subsequently end in agglomerations. The pulverulent concentrate, which is often stored for months, is made up *in situ* with water and sulfuric acid before coppering, and the coppering bath is in many cases maintained ready for use over several weeks and is replenished as necessary. The pulverulent concentrate often requires prolonged stirring or agitation and possibly heating to a slightly elevated temperature, such as for example up to 60°C. Since the coppering bath is however normally kept and used in premises that can be heated as necessary, there is normally no need for the bath to be stable with regard to freezing and thawing. Furthermore the requirements as regards the industrial use

also of concentrates and baths for coppering are becoming increasingly stringent.

On account of the often months-long storage and the in some cases fairly long transportation of concentrates to the currentless coppering and bronzing site, there was a need to develop a concentrate that can be stored if possible for several months and that can be transported without any problem in various climatic regions. In the case of a liquid concentrate a concentrate has to be developed that also does not cause any problems as regards freezing and thawing, since once coppering solutions have been frozen they no longer independently form homogeneous solutions. Also, an addition of antifreeze agents does not help since the salts precipitate in any case and form a floor sediment. Accordingly in practice virtually only pulverulent concentrates or, in exceptional cases, two-component concentrates are produced with copper sulfate solution as well as with a separately stored liquid mixture of brightening agent and other sensitive liquids. Up to now no liquid concentrate for currentless coppering or bronzing is known to the Applicant that contains all or virtually all the components needed for coppering or bronzing.

In addition the object existed of providing a concentrate and a process for currentless coppering or bronzing that is as environmentally friendly as possible and that moreover has as safe a pH value as possible. These concentrates should in addition be able to be used easily, without complications and efficiently for the coppering or bronzing. The concentrate should have as high a copper content as possible. The bath prepared from the concentrate *inter alia* by dilution should form high-gloss,

solid, firmly adhering copper coatings. It would be advantageous if this concentrate were to contain all the components for the currentless coppering or bronzing.

It has been established that an aqueous copper-rich concentrate in which a large part of the copper content is present in complexed form can exist as a solid homogeneous mass below the freezing point and can rapidly re-form into a homogeneous aqueous mixture on thawing, without having to be stirred or agitated.

This object is achieved with an aqueous concentrate that is stable on freezing and thawing that contains at least one water-soluble or water-dispersible copper compound and optionally also a water-soluble or water-dispersible tin compound for use in the diluted state as a bath for the currentless coppering or bronzing of objects, in particular metallic objects such as for example iron or steel wires, which is characterised in that, starting from basic copper carbonate and complex-forming agent(s), it contains at least one complexed water-soluble or water-dispersed copper compound formed therefrom, and optionally also a residue of basic copper carbonate.

Preferably all compounds present in the concentrate are dissolved or dispersed in water. The complexing agent may be contained in stoichiometric amount, in a sub-stoichiometric amount or in excess. Preferably the concentrate contains a basic copper carbonate or at least one compound formed therefrom by complexing with a complex-forming agent. On account of the complexing a high copper content can be maintained in the solution without precipitation occurring.

The mixture may be repeatedly frozen at low temperatures down to at least -14°C and may be thawed without the quality of the mixture, in particular the quality of the coppering bath prepared therefrom, being adversely affected. This mixture normally serves as a concentrate that can be transported as a liquid product and that by dilution and optionally by addition of individual additives can be made up into a coppering bath, or

10, particularly preferably in the range from 6 to 9, and most particularly preferably in the range from 7 to 8. The adjustment may be made *inter alia* with at least one base such as for example NaOH, KOH and NH_4OH and/or with at least one amine. If the concentrate has a pH of about 7, it may be termed as dermatologically neutral.

The concentrate advantageously contains at least one copper compound that is at least partially complexed with a complexing agent based on at least one monohydroxycarboxylic, dihydroxycarboxylic, trihydroxycarboxylic and/or polyhydroxycarboxylic acid, phosphonic acid, diphosphonic acid and/or chemically related compound and/or at least one of their derivatives.

The object of the present invention is also achieved with an aqueous bath containing at least one water-soluble or water-dispersible copper compound and optionally also a water-soluble or water-dispersible tin compound for the currentless coppering or bronzing of objects, in particular metallic objects such as for example iron-containing wires, which is characterised in that, starting from basic copper carbonate and complex-forming agent(s), it contains at least one complexed water-soluble or water-dispersed copper compound formed therefrom, at least one brightening agent and optionally also a residue of basic copper carbonate, and that the said bath is adjusted to a pH value of less than 2.5.

Preferably all compounds present in the bath are dissolved or dispersed in water. An addition of tin and optionally generally minor amounts of other alloying constituents may advantageously be made in the form of water-soluble or water-dispersed compounds such as tin hydroxide, tin carbonate and/or at least one organotin

compound such as for example at least one tin alcoholate or similar compounds of the further alloying constituents that are possibly used in the preparation of the bath, i.e. starting from the concentrate. The amount of tin added to the bath may in particular be in the range from 0.03 to 8 g/l Sn. The concentrate and/or bath according to the invention is preferably free or largely free of cyanides, diphosphates, phosphates,

Patent Claims

1. Aqueous concentrate stable on freezing and thawing and containing at least one water-soluble or water-dispersible copper compound and optionally also a water-soluble or water-dispersible tin compound, for use in the diluted state as a bath for the currentless coppering or bronzing of objects, in particular metallic objects such as for example iron or steel wires, characterised in that, starting from basic copper carbonate and complex-forming agent(s), the concentrate contains at least one complexed water-soluble or water-dispersed copper compound formed therefrom and optionally also a residue of basic copper carbonate.

2. Aqueous concentrate according to claim 1, characterised in that at least 40 wt.% of the contained copper compounds are complexed.

3. Aqueous concentrate according to claim 1 or 2, characterised in that the at least one copper compound is at least partially complexed with a complex-forming agent based on at least one complexing monohydroxycarboxylic, dihydroxycarboxylic, trihydroxycarboxylic and/or polyhydroxycarboxylic acid and/or at least one of their derivatives.

4. Aqueous concentrate according to one of the preceding claims, characterised in that it is stable to freezing and thawing down to at least -8°C.

5. Aqueous concentrate according to one of the preceding claims, characterised in that it has a copper content in the range from 3 to 200 g/l Cu.

6. Aqueous concentrate according to one of the preceding claims, characterised in that it is adjusted to a pH value in the range from 4 to 11.

7. Aqueous concentrate according to one of the preceding claims, characterised in that the at least one copper compound is at least partially complexed with a complexing agent based on at least one monohydroxycarboxylic, dihydroxycarboxylic, trihydroxycarboxylic and/or polyhydroxycarboxylic acid, phosphonic acid, diphosphonic acid and/or at least one of their derivatives.

8. Aqueous bath containing at least one water-soluble or water-dispersible copper compound and optionally also a water-soluble or water-dispersible tin compound, for the currentless coppering or bronzing of objects, in particular metallic objects such as for example iron-containing wires, characterised in that, starting from basic copper carbonate and complex-forming agent(s), the bath contains at least one complexed water-soluble or water-dispersed copper compound formed therefrom, at least one brightening agent and optionally also a residue of basic copper carbonate, and that it is adjusted to a pH value of less than 2.5.

9. Aqueous bath according to claim 8, characterised in that at least 40 wt.% of the contained copper compounds are complexed.

10. Aqueous bath according to claim 8 or 9, characterised in that it has a copper content in the range from 0.05 to 120 g/l.

11. Aqueous bath according to one of claims 8 to 10, characterised in that the iron content of the bath is up to at least 90 or even up to at least 110 g/l Fe^{2+}.

12. Aqueous bath according to one of claims 8 to 11, characterised in that the at least one copper compound is a compound that is at least partially complexed with a complex-forming agent based on at least one complexing monohydroxycarboxylic, dihydroxycarboxylic, trihydroxycarboxylic and/or polyhydroxycarboxylic acid, phosphonic acid, diphosphonic acid and/or at least one of their derivatives.